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1. Title of the Invention

Alkaline Battery

2. Scope of Demand for Patent

(1) An alkaline battery comprising an alkaline electrolyte and a zinc negative electrode, said zinc negative electrode comprising a zinc powder which is free from mercury, cadmium and lead, said zinc powder comprising zinc particles having adhered on the surfaces thereof bismuth in an amount of 0.005 – 0.5 wt% based on the amount of zinc powder, said zinc negative electrode further comprising a fluorine type surfactant in an amount of 0.05 wt% based on the amount of zinc powder.

3. Detailed Description of the Invention

[0001]

[Industrial Field of Application]

This invention relates to an alkaline battery. In particular, the invention relates to an alkaline battery which employs as a negative electrode (anode) active material a zinc powder which is free from mercury, cadmium and lead.

[0002]

An alkaline battery using zinc as a negative electrode (anode) active material generates a hydrogen gas during its storage or after its partial discharge. This is due to the corrosion of zinc. For this reason, in a conventional alkaline battery, a zinc powder which is alloyed with lead, indium, bismuth, aluminum, etc, and the surface of which is amalgamated with mercury in an amount of 0.15 to 0.6 wt% based on the amount of zinc has heretofore been used. Such modification of zinc powder has been

made to suppress the evolution of hydrogen within a cell by reducing the hydrogen over-voltage of zinc.

[0003]

In order to meet the recent public desire of the low or no pollution of the environment, it is proposed to manufacture such an alkaline battery as one that uses zinc which is free from mercury, cadmium and lead, and onto the surfaces of its particles indium is adhered and at the same time an organic compound is added to the alkaline battery to suppress the hydrogen gas evolution within the battery.

[0004]

[Problems to be Solved by the Invention]

However, with respect to an alkaline battery that uses a gel-sate zinc negative electrode prepared by a zinc powder on the surface of which is adhered indium, there is a problem as follows,

In proportion to the amount of indium adhered on the surfaces of the zinc powder particles, viscosity of the gel-state zinc negative electrode increases. As a result, when a cylindrical separator is filled with the gel-state zinc negative electrode during the process of battery production, the amount of the gel-state zinc negative electrode filled in the cylindrical separator becomes uneven, and in turn the discharge characteristics of the batteries becomes uneven.

[0005]

The reason for this phenomena is considered to be as follows.

The indium particles adhered on the surfaces of zinc powder articles may act as a binder to join zinc powder particles one another. Mercury also shows the same function. However, since indium is solid, it shows different function than mercury and makes sliding ability among the zinc powder particles poorer. As a result, viscosity of the gel-state zinc negative electrode increases and in turn the filling amount of the gel-state zinc negative electrode becomes uneven.

[0006]

This invention has been accomplished to overcome the above mentioned problem. The object of the invention is to restrict the increase of viscosity of the gel-state zinc negative electrode and to provide no pollution alkaline batteries that show a small amount of gas evolution and shows small scattering with respect to the discharge characteristics.

[0007]

[Means to Solve the Problems]

To attain the object mentioned above, the present invention provides an

alkaline battery which comprises an alkaline electrolyte and a zinc negative electrode, wherein said zinc negative electrode is free from mercury, cadmium and lead, and wherein 0.005 - 0.5 wt% based on the amount of zinc powder of bismuth is adhered on the surfaces of zinc powder particles, and wherein fluorine-containing surfactant in an amount of 0.05 wt% based on the amount pf zinc power is contained in the gel-state zinc negative electrode.

[0008]

[Works or Operation]

According to the present invention bismuth rather than indium has been adhered on the surfaces of particles of zinc which is used in an alkaline battery. Different from the case when indium is used, the joining of zinc particles can be avoided. Accordingly, viscosity increase of the gel-state zinc negative electrode observed in the case of indium addition can be avoided. Thus, scattering of the filling amount of the gel-state zinc anode into the cylindrical separator observed during the process of battery production in the case of indium addition can be avoided. Accordingly, there is a small scattering with respect to the discharge characteristics. Since bismuth shows anti-corrosion characteristics just like indium does, it has become possible to obtain an alkaline battery which evolves a decreased amount of hydrogen gas.

[0009]

How to adhere bismuth onto the surfaces of zinc particles is as follows.

Zinc is dispersed in a weakly acidic aqueous solution, to which an aqueous solution of water soluble bismuth salt is added dropwise, so that displacement of zinc with bismuth may be occurred on the surfaces of zinc particles due to the difference in ionizing abilities. The amount of bismuth to adhere onto the surface of zinc particle is preferably between 0.005 wt% and 0.5 wt% based on the amount of zinc powder. Even if out of this range, no increase in viscosity of the gel-state zinc anode will be observed. However, the effect of suppressing gas evolution decreases, if the amount of bismuth adhering on the zinc particle surface is out of the above mentioned range.

[0010]

The fluorine type surfactant for aiding the suppression of gas evolution by means of bismuth addition was added to the gel-state zinc anode after its being diluted with water so that its amount may become 0.05 wt% or less based on the amount of zinc powder.

Even if the amount of addition thereof is small, substantial effect of addition can be observed. However, if the amount of its addition exceeds 0.05 wt%, discharge characteristics will be impaired, though the effect of suppressing gas evolution

increases.

[0011]

[Examples] The present invention will be described in detail based on the working Examples.

[Example 1]

First, 1 kg of zinc powder which is free from mercury, cadmium and lead and which contains 0.05 wt% bismuth, 0.05 wt% indium and 0.01 wt% aluminum and which has a particle size within the range of 100 - 300μm was prepared. A 1 kg amount of this zinc powder was put into a 1 wt% aqueous solution of sulfuric acid, to which, with agitation, 50 ml of a 1 wt% aqueous solution of nitric acid (containing 1 mg of bismuth in 1 ml of the aqueous nitric acid solution) was added by dropwise, so that bismuth might be uniformly deposited on the surfaces of zinc particles by making use of the difference in ionizing abilities of zinc and bismuth, followed by dehydrating and drying. The resulting zinc powder is theoretically admitted to have adhered on the surface thereof 0.005 wt% of bismuth.

To 65 parts by weight of this zinc powder was added 0.6 part by weight of poly acrylic acid as a gelling agent, and the mixture was uniformly agitated by a conventional mixer, followed by gradually adding the resulting mixture to 35 parts by weight of an aqueous 35 wt% solution of potassium hydroxide to which 3.5 wt% of zinc oxide had been dissolved, with agitation being given to the total mixture. By means of this agitation a gel-state uniform mixture was obtained. Further, as a fluorine type surfactant, a 1wt% solution of perfluorolkylethylene oxide adduct was added to the final mixture so that the content of said adduct might become 0.005 wt% based on the amount of zinc powder, followed by agitation, mixing to prepare a uniform, gel-state zinc negative electrode.

[0012]

By using the gel-state zinc anode thus obtained, R6-type (No. 3) alkaline battery (JIS based) as shown in Fig.1 was prepared. In the same figure, reference number 1 represents a metal-made cylindrical vessel (can) having a bottom which also may function as a positive electrode terminal.

This metal-made can 1 is filled up with a cylindrically press-molded positive electrode mixture 2. The positive electrode mixture 2 has been prepared by mixing a powder of manganese dioxide and a powder of carbon, placing the resulting mixture within the metal-made can 1 and pressure-molding the mixture with a predetermined pressure into a hollow, cylindrical body. The hollow space within the positive electrode mixture 2 is filled up with the gel-state zinc negative electrode 4 prepared by the above

mentioned process, having been intervened by a cylindrical, bottom closed separator made of a nonwoven cloth of acetal-polyvinylalcohol fiber. Within the gel-state zinc negative electrode 4, a brass-made negative electrode current collecting bar 5 is placed inserted into the gel-state negative electrode 4, with its one edge being protruded from the gel-state negative electrode 4. An insulating gasket 6 having a cross-section in a double ring-shape made of a polyamide resin is provided in contact with the position of the outer peripheral surface of the projected portion of the negative electrode current collector 4 and also in contact with the inner peripheral surface of the upper portion of the metal-made can 1. A ring-shaped metal plate 7 is provided between the double ring portion of said insulating gasket 6. A metallic sealing plate 8 having a shape of a cap which also acts as a negative electrode terminal is provided between the double ring portion of said insulating gasket 6, in such a manner that it may contact a head portion of said current collecting bar 5. By bending the opening edge of the metal-made can 1 towards the inside thereof, the can 1 is sealed by the aid of the gasket 6 and the metal-made sealing plate 8.

[0013]

[Examples 2 - 4]

Samples of JIS-standard LR6-type alkaline batteries (No. 3 type) were prepared by repeating the same procedures as in the case of Example 1, except that the amounts of bismuth adhesion were varied (0.01 wt%, 0.1 wt% and 0.5 wt% based on the amount of zinc powder, wherein, in each run, 100 ml of a 1 wt% aqueous nitric acid solution having bismuth content each of 1 mg, 10 mg and 50 mg per 1 ml in the 1 wt% aqueous nitric acid solution was used.)

[0014]

[Examples 5 - 8]

JIS-based R6-type (No. 3 type) alkaline batteries as the sample of Examples 5 - 8 were prepared by repeating the procedures of Example 1, except that the amount of bismuth adhered to zinc particles was determined to be 0.1 wt% based on the amount of zinc powder and the addition amounts of the fluorine type surfactant were 0.001 wt%, 0.0005 wt%, 0.01 wt% and 0.05 wt% based on the amount of zinc powder.

[0015]

[Comparative Examples 1 - 4]

JIS-based R6-type (No. 3) alkaline batteries as the samples of Comparative Examples 1 - 4 were prepared by repeating the procedures of Example 1 except that indium rather than bismuth was coated on zinc in an amount of 0.005 wt%, 0.01 wt% or 0.1 wt% based on the amount of zinc powder. For this purpose, 100 ml each of a 1 wt%

aqueous nitric acid solution containing, per 1 ml of the aqueous solution, 0.5 mg, 1 mg, 10 mg or 50 mg of indium was used so that 0.005 wt%, 0.01 wt%, 0.1 wt% or 0.5 wt% of indium based on the amount of zinc powder could be adhered on the zinc particles.

[0016]

[Comparative Example 5]

JIS-based R6 type (No. 3) alkaline cell as a sample of Comparative Example 5 was prepared by repeating the procedures of Example 1 except that zinc powder containing 0.15 wt% of mercury, 0.05 wt% of lead, 0.05 w% of bismuth and 0.02 wt% of indium and having a particle size within the range of 100 - 300 μm was used, with no fluorine-system surfactant being used.

[0017]

[Examples 6, 7]

JIS-based LR6-type (No. 3) alkaline batteries as samples of Examples 6 and 7 were prepared by repeating the procedures of Example 1 except that 100 ml of a 1 wt% aqueous nitric acid solution containing 0.1 mg or 100 mg of bismuth per 1 ml of the aqueous solution was used for the purpose of adhering 0.001 wt% or 1.0 wt% of bismuth based on the amount of zinc powder would be coated on zinc powder.

[0018]

[Comparative Example 8]

JIS-based LR6-type (No. 3) alkaline battery as a sample of Comparative Example 8 was prepared by repeating the procedures of Example 1 except that the adhesion amount of bismuth was 0.1 wt% based on the amount of zinc powder and the addition amount of the fluorine type surfactant was 0.1 wt% based on the amount of zinc powder.

[0019]

In each of the Examples and Comparative Examples, 100 of battery samples were prepared. That is, 900 batteries were prepared in total. For each of these sample batteries, the weights of the battery before and after filling its cylindrical separator with a gel-state zinc anode material were measured, and the filling amount of the gel-state zinc anode material was determined by calculation from the difference in weights.

[0020]

Similarly, ten battery samples per each Examples were prepared to obtain 90 samples in total. For each of the sample batteries, continuous discharge was conducted under load resistance of 10 Ω at 20 ℃ until static voltage became 0.9 V to determine the discharge maintenance time.

[0021]

Similarly, twenty battery samples per each Example were prepared to obtain 180 samples in total. Sample batteries were stored in a constant temperature vessel kept at 60 ℃. Ten samples per each Example were taken out of the vessel after one month storage in the constant temperature vessel. Another ten samples per each Example were taken out of the constant temperature vessel after three months' storage. Hydrogen gas that evolved by the decomposition of anode material in water during the storage time was collected and measured. The results are shown in Table 1 and Table 2 given hereinbelow. As is obvious from Tables 1 and 2, the batteries prepared by using the gel-state zinc anode material prepared according to the manner shown in Examples 1- 8 showed smaller scattering in the filling amounts of the gal-state zinc anode material than in the cases of Comparative Examples 1 – 4. Accordingly, the discharge maintenance time measured under load resistance of 10Ω and at 20 ℃ also exhibited smaller scattering.

[0022]

This means that the gel-state zinc anode material prepared in Examples 1 – 8 shows a small scattering with respect to the filling amounts into the cylindrical separator. This is because the gel-state zinc anode material consisting of the bismuth coated zinc powder particles having the improved fluidity is used. Due to the presence of bismuth on the surfaces of the particles, the coagulation of zinc particles often caused in the case of indium coated zinc particles can be avoided. As a result, viscosity increase does not appear when the gel-state zinc anode material is prepared by using bismuth coated zinc particles according to the present invention. Since the scattering of the amounts of the gel-state anode material filled in the cylindrical separator became smaller, the scattering of the discharge maintenance time also became smaller. In addition, if the amounts of gas evolution are compared between the cases of Comparative Examples 6 – 7 (Prior Art) and Examples 1 - 4 (Present Invention), a larger amount of gas evolution is observed in the cases of Comparative Examples. This means that the present invention correctly teaches the amount of bismuth to be coated on the surfaces of zinc particles, which amount is in the range of 0.005 wt% - 0.5 wt% based of the amount of zinc powder. When the battery of Comparative Example 8 is compared with the batteries of Examples 5 and 6, it is understood that when the amount of addition of a fluorine type surfactant is 0.1 wt% based on the amount of zinc powder (Comparative Example 8), the scattering of the filling amounts of the gel-state zinc anode material are almost the same, but , with respect to the amount of gas evolution, slightly better result is obtained in the case of Comparative Example 8 but the discharge maintenance time is short in the case of Comparative Example. When

the amount of using the fluorine type surfactant is very small as in the case of Example 6, the amount of gas evolution relatively increases, though it is advantageous from the viewpoint of minimizing the scattering of the filling amount and the discharge maintenance time. This means that the addition rate of the fluorine type surfactant should be 0.05 wt% or less and that if more amount is added, the discharge maintenance time will be shortened.

[0023]

Table 1

	Amount of adhesion of corrosion proof material wt(%)	Amount of addition of fluorine type surfactant (wt%)	Filling up amount of gel-state zinc anode material (g)	Discharge maintenance time (hour)	Amount of gas evolution in storage at 60℃ (cc)	
					After 1 month	After 3 months
Example 1	Bi : 0.005	0.005	5.7 (5.6 - 5.8)	17.5 (17.2 - 17.8)	1.0 (0.9 - 1.2)	2.1 (2.0 - 2.3)
2	0.01	0.005	5.7 (5.6 - 5.8)	17.4 (17.3 - 17.8)	0.9 (0.8 - 1.1)	2.0 (1.9 - 2.2)
3	0.1	0.005	5.7 (5.6 - 5.8)	17.5 (17.3 - 17.8)	0.9 (0.8 - 1.0)	2.0 (1.8 - 2.1)
4	0.5	0.005	5.7 (5.5 - 5.8)	17.4 (17.3 - 17.7)	1.0 (0.8 - 1.1)	2.0 (1.9 - 2.1)
Example 5	Bi : 0.1	0.001	5.7 (5.6 - 5.8)	17.4 (17.2 - 17.8)	0.9 (0.8 - 1.0)	2.0 (1.9 - 2.1)
6	0.1	0.0005	5.7 (5.6 - 5.8)	17.5 (17.2 - 17.8)	1.1 (0.9 - 1.4)	2.3 (2.1 - 2.5)
7	0.1	0.01	5.7 (5.6 - 5.8)	17.5 (17.2 - 17.8)	0.9 (0.8 - 1.0)	2.0 (1.8 - 2.1)
8	0.1	0.05	5.7 (5.6 - 5.8)	17.4 (17.2 - 17.7)	0.8 (0.7 - 1.0)	1.9 (1.8 - 2.0)

[0024]

Table 2

	Amount of adhesion of corrosion proof material wt(%)	Amount of addition of fluorine type surfactant (wt%)	Filling up amount of gel-state zinc anode material (g)	Discharge maintenance time (hour)	Amount of gas evolution in storage at 60°C (cc)	
					After 1 month	After 3 months
Comparative Example 1	In : 0.005	0.005	5.7 (5.5 - 5.8)	17.5 (17.0 - 17.9)	1.0 (0.9 - 1.1)	2.1 (1.9 - 2.2)
2	0.01	0.005	5.7 (5.4 - 5.8)	17.5 (16.8 - 17.9)	0.9 (0.8 - 1.1)	2.0 (1.9 - 2.1)
3	0.1	0.005	5.7 (5.3 - 5.8)	17.3 (16.5 - 18.0)	1.0 (0.8 - 1.1)	2.0 (1.8 - 2.1)
4	0.5	0.005	5.6 (5.2 - 5.9)	17.1 (16.0 - 18.3)	1.1 (0.9 - 1.2)	2.1 (2.0 - 2.2)
Comparative Example 5	0	0	5.7 (5.6 - 5.8)	17.5 (17.3 - 17.8)	1.0 (0.9 - 1.2)	2.1 (1.9 - 2.2)
Comparative Example 6	Bi : 0.001	0.005	5.7 (5.6 - 5.8)	17.5 (17.3 - 17.8)	1.4 (1.3 - 1.5)	3.1 (2.9 - 3.2)
7	1.0	0.005	5.7 (5.6 - 5.8)	17.2 (17.0 - 17.5)	1.5 (1.3 - 1.6)	3.2 (3.1 - 3.4)
Comparative Example 8	0.1	0.1	5.7 (5.6 - 5.8)	16.5 (16.2 - 16.9)	0.9 (0.8 - 1.0)	1.9 (1.8 - 2.0)

[0025]

The batteries of Examples 1 – 8 are recognized to be almost equal to the battery of Comparative Example 5 with respect to any of the scattering degree of the filling amount of the gel-state zinc anode material, discharge maintenance time and the amount of gas evolution. Accordingly, they are by no means inferior to the conventional amalgamated battery prepared by using zinc powder containing 0.15wt% mercury, 0.05 wt% lead, 0.05 wt% bismuth and 0.02 wt% indium.

[0026]

[Effect of the Invention]

As explained above, the present invention provides no pollution alkaline batteries having a small scattering of discharge maintenance time and a small amount of gas evolution.

[Explanation of the Reference Numerals]

1 ······ metal-made can 2 ······ positive electrode mixture

3 ······ separator 4 ······ gel-state negative electrode

5 ······ negative electrode current collecting bar

6 ······ insulating gasket 7 ······ metal plate

7 ······ metal plate for sealing